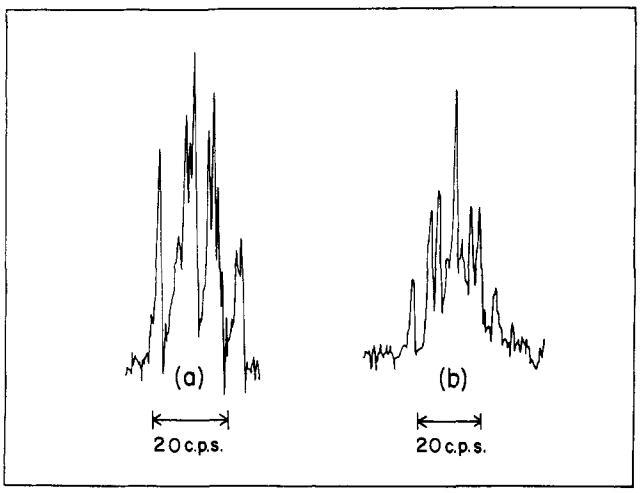


Figure 1. Room-temperature F^{19} spectra of mF_3 (a) and pF_3 (b).

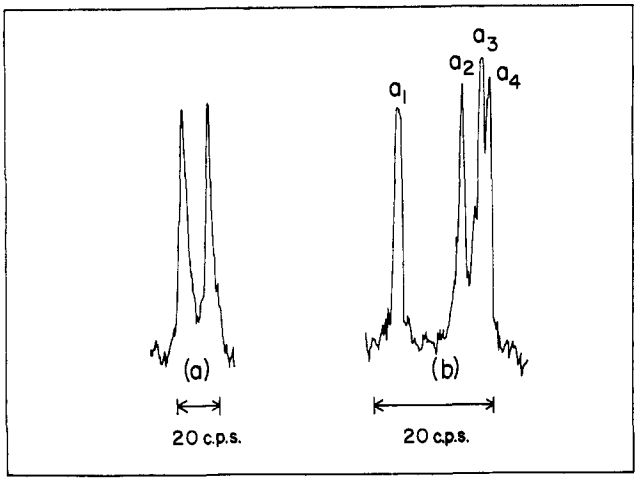


Figure 2. Low-temperature decoupled F^{19} spectra of mF_3 (a) and mF_2 (b).

We may then assign the low-field line of the mF_3 doublet to fluorines e′ and e″ and the high-field line to fluorines d and e‴. We may assign line a_1 of the four-line mF_2 spectrum to fluorine a, a_2 and a_3 to fluorines c′ and c″, and a_4 to fluorine b.

For either conformation II or III above, the presence of more nonequivalent fluorines than appear to be present would be required; furthermore, the mF_1 and pF_3 species would be expected to show nonequivalent fluorines. In addition, the temperature variation of the decoupled mF_2 and mF_3 spectra may be quantitatively explained on the basis of the propeller conformation and the spectral assignments given above.[1]

The chemical shifts of the F^{19} lines at room temperature are given in Table I. An interpretation of these shifts and analyses of the proton n.m.r. spectra of these ions will be published.

and to fluorines d and e‴ should be approximately the same, *viz.*, zero. This effect should be much larger (but nearly the same) for fluorines a, e′, and e″, since the pairs of fluorines involved are near neighbors. The second effect is that produced by the ring current of the adjacent phenyl rings. The principal ring current effect will be that of the closer of the two rings to the fluorine in question (*e.g.*, for fluorine b the unsubstituted ring) and will depend slightly on whether the ring is substituted or not. Thus, this effect should give a different contribution to the shieldings of fluorines c′ and c″ while it would give essentially the same contribution to fluorines d, e′, e″, and e‴.

Table I. Room Temperature F^{19} Chemical Shifts

Ion	Chemical shift, p.p.m.[a]	Ion	Chemical shift, p.p.m.[a]
pF_1	8.72	mF_1	34.7
pF_2	9.24	mF_2	34.0
pF_3	9.77	mF_3	33.3

[a] Relative to trifluoroacetic acid internal standard.

Acknowledgment. We wish to thank the National Science Foundation for financial support and Drs. Axsel A. Bothner-By and John A. Pople for stimulating discussions.

Allan K. Colter, Ingeborg I. Schuster, Robert J. Kurland
Department of Chemistry, Carnegie Institute of Technology
Pittsburgh, Pennsylvania 15213
Received February 24, 1965

Fluorine Magnetic Resonance Studies of Conformational Interconversion Rates in Triphenylcarbonium Ions

Sir:

The temperature variation of the decoupled F^{19} n.m.r. spectra of 3,3′-difluoro- and 3,3′,3″-trifluorotriphenylcarbonium ions (mF_2 and mF_3, respectively) has been used to obtain interconversion rates between the conformers discussed in the preceding communication.[1]

At about −30° the single line of the decoupled mF_3 spectrum broadens, splitting into two lines of equal intensity as the temperature is lowered; this doublet separation increases to a limiting value of 11.4 c.p.s. as the temperature is lowered to −51°, remaining unchanged down to −80° (Figure 1). The mF_2 line

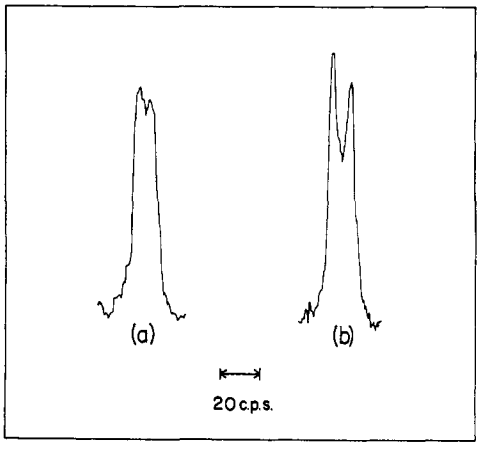


Figure 1. Decoupled F^{19} spectrum of mF_3 at (a) −31.0°, (b) −37.7°.

broadens at about −38°, splitting into a doublet of 3:1 intensity ratio; the separation of these lines increases as the temperature is lowered, the larger of these lines (a in Figure 2a) splitting into two lines of intensity ratio 2:1 at −57° (Figure 2b). The stronger of these two lines (aa_1 in Figure 2b) splits into a barely resolved doublet at −59° (Figure 2c); this four-line pattern remains unchanged down to −80°.

(1) A. K. Colter, I. I. Schuster, and R. J. Kurland, *J. Am. Chem. Soc.*, **87**, 2278 (1965).

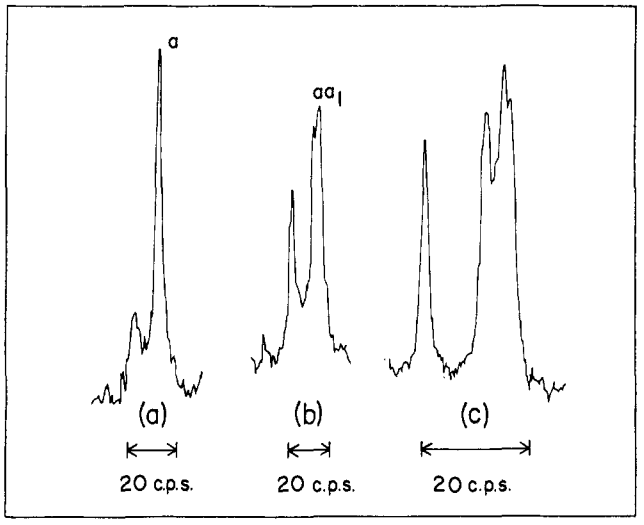


Figure 2. Decoupled F^{19} spectrum of mF_2 at (a) −42.8°, (b) −57.1°, (c) −59.0°.

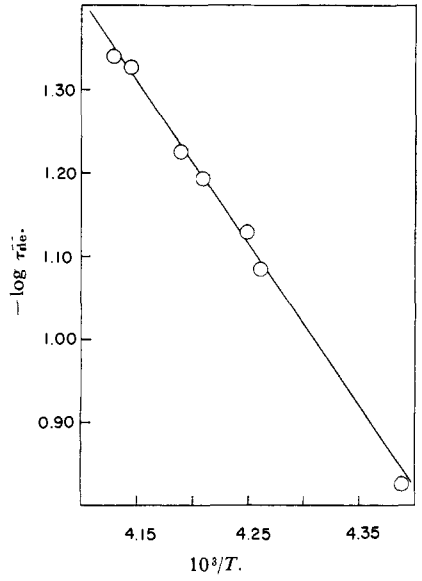


Figure 3. Plot of $-\log \tau_{\bar{d}\bar{e}}$ *vs.* $1/T$ for mF_3.

Interconversion between the conformers pictured in ref. 1 (A, B, and C of mF_2, D and E of mF_3) can occur when one or more rings "flip," *i.e.*, rotate about the

$$\tau_{ac'} = \tau_{c'a} = \tau_{ac''} = \tau_{c''a} = \tau_{bc'} = \tau_{c'b} = \tau_{bc''} = \tau_{c''b} = 1/(k_1 + k_2) \quad (1a)$$

$$\tau_{ab} = \tau_{ba} = \tau_{c'c''} = \tau_{c''c'} = 1/(k_2 + k_3) \quad (1b)$$

$$\tau_{de'} = \tau_{e'd} = \tau_{de''} = \tau_{e''d} = \tau_{dc'''} = \tau_{c'''d} = \tau_{e'c''} = \tau_{e''e'} = \tau_{e'e'''} = \tau_{e'''e'} = 1/(k_1 + k_2) \quad (1c)$$

$$\tau_{e''e'''} = \tau_{e'''e''} = 1/(k_2 + k_3) \quad (1d)$$

bond to the central carbon, passing through a plane perpendicular to that formed by the three central carbon–phenyl bonds. In order to retain the required propeller conformation, the rings which do not flip must necessarily invert (more or less simultaneously) by passing through the plane of the central carbon–phenyl bonds. Denoting by k_1, k_2, and k_3 the probabilities per unit time per molecule that one, two, or three rings, respectively, flip, the following expressions for τ_{ij}, the mean lifetime a fluorine spends at a site i before jumping to site j, can be derived.

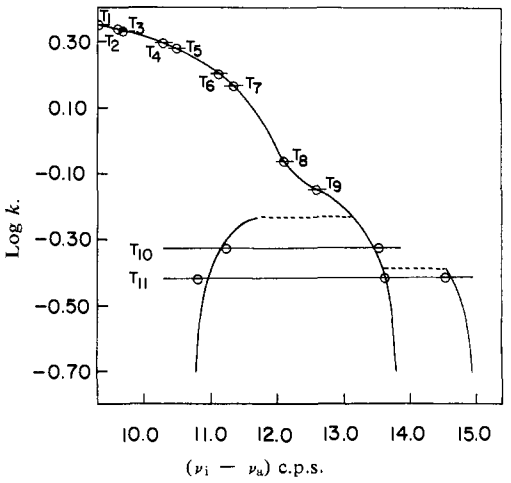


Figure 4. Plot of log k *vs.* calculated peak positions for F_2. Experimental points shown by circles.

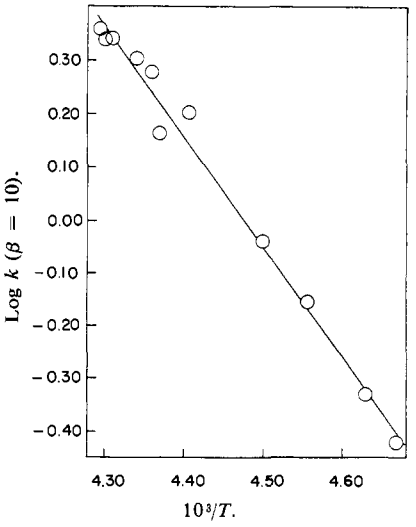


Figure 5. Plot of log k *vs.* $1/T$ for mF_2.

The designation of nonequivalent fluorines in eq. 1 is that given in ref. 1. It has also been assumed that k_1, k_2, and k_3 are the same for all conformers and are the same for substituted and unsubstituted rings.

If, as suggested,[1] fluorines d and e''' in mF_3 are effectively equivalent, as are e' and e'', then the mean lifetime $\tau_{\bar{d}\bar{e}}$ is given by

$$1/\tau_{\bar{d}\bar{e}} = 1/\tau_{\bar{e}\bar{d}} = 1.5k_1 + 2k_2 + 0.5k_3 \quad (2)$$

where $\bar{d}$ denotes the equivalent pair d and e''' and $\bar{e}$ denotes the equivalent fluorines e' and e''.

The line shape behavior for exchange between several sites can be analyzed by means of modified Bloch equations.[2] For the case where fluorine pairs d, e''' and e', e'' of mF_3 are treated as equivalent, one may obtain an explicit formula for the over-all rate constant, $1/\tau_{\bar{d}\bar{e}}$, formally similar to that for exchange between two sites.[3,4]

(2) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, N. Y., 1959, p. 224.
(3) Reference 2, eq. 10-31, p. 224.

A plot of log $\tau_{\bar{d}\bar{e}}$ *vs.* $1/T$ (°K.) is shown in Figure 3; the slope of the best fit straight line through the experimental points leads to an activation energy of 9.1 kcal. mole^{-1} for the interconversion.

The more complicated line shape formula derived for mF_2 is a function of the two rate parameters k and β, defined as

$$k = k_1 + k_2 \quad (3a)$$

$$\beta = (k_2 + k_3)/(k_1 + k_2) \quad (3b)$$

The parameter β is assumed to be approximately constant over the temperature range of interest.

A computer program was used to construct plots of log k *vs.* the calculated peak positions for given values of β. By interpolation, these plots yielded values of k corresponding to the temperatures of the observed peak positions (Figure 4). Values of β ranging from 6 to 20 gave essentially linear plots of log k *vs.* $1/T$ (Figure 5) corresponding to activation energies[5] from 9.4 to 9.6 kcal. mole^{-1}.

From eq. 2, 3a, and 3b it is possible to show that the relation

$$1/(k\tau_{\bar{d}\bar{e}}) = 0.5(3 + \beta) \quad (4)$$

should hold if, indeed, k_1, k_2, and k_3 are the same for mF_2 and mF_3. For $\beta = 10$, $1/(k\tau_{\bar{d}\bar{e}}) = 5.0$ (at a common temperature), whereas from eq. 4 $1/(k\tau_{\bar{d}\bar{e}})$ should equal 6.5. However, the analysis is sufficiently insensitive to the value of β chosen that we consider the identity of k_1, k_2, and k_3 for mF_2 and mF_3 to have been demonstrated. Further, the correctness of the model conformations and interconversion scheme is supported by the identity of the derived activation energies for mF_2 and mF_3. The large value of β (6 to 20) indicates that the three-ring flip probability, k_3, is much larger than k_1 or k_2. A detailed report of this work will be published, along with an analysis of the proton n.m.r. spectra of these compounds.

Acknowledgment. We wish to thank the National Science Foundation for financial support.

(4) The more general formula for the line shape of mF_3 obtained under the assumption that the chemical shifts between d and e''' and between e' and e'' are 0.4 c.p.s. yields similar results.

(5) Calculated energies of activation are considered accurate to about ±0.5 kcal. mole^{-1}.

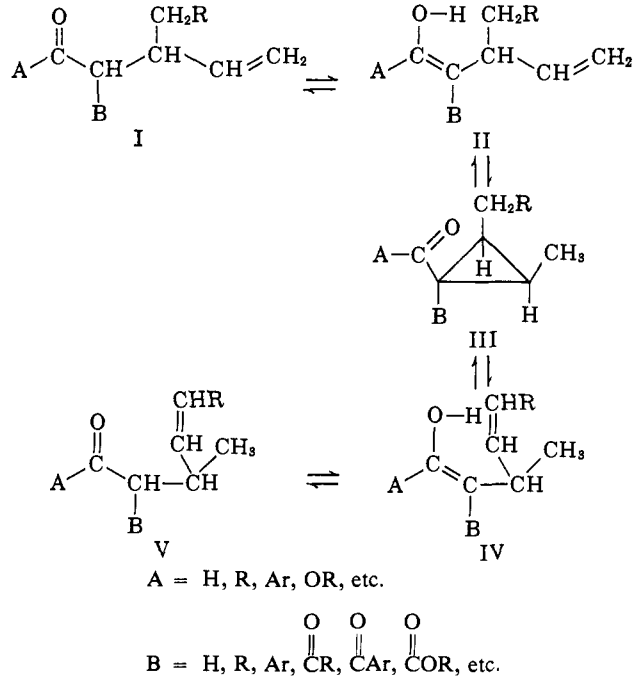
Robert J. Kurland, Ingeborg I. Schuster, Allan K. Colter
Department of Chemistry, Carnegie Institute of Technology
Pittsburgh, Pennsylvania 15213
Received February 24, 1965

Thermal Rearrangement of Cyclopropyl Ketones to Homoallylic Ketones. Relationship to the "Abnormal Claisen Rearrangement"

Sir:

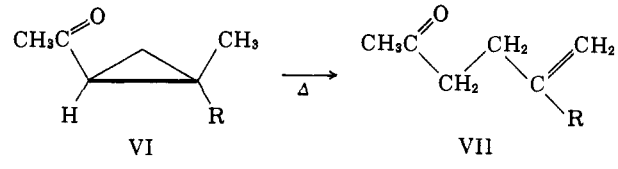
The "abnormal Claisen rearrangement"[1] has now been quite clearly identified as the result of two consecutive processes: the normal *ortho* Claisen rearrangement of a γ-alkylallyl phenyl ether to an *o*-(α-alkylallyl)-phenol, followed by an isomerization of the side chain of this phenol.[2] The mechanism of the secondary isomerization has been formulated as involving a cyclopropyldienone intermediate.[2,3] Assuming this mechanism is correct, we anticipate that such a mechanism may not be restricted to phenols but may represent quite a general, and so far unnoticed, type of intramolecular rearrangement.

In simplest form, it may be outlined as the conversion of one homoallylic carbonyl compound (I) to another (V) *via* the allylic enols II and IV and the cyclopropyl



carbonyl compound III. We now wish to report the thermal rearrangement of two cyclopropyl ketones to homoallylic ketones (*e.g.*, III → I) and, in the following communication,[4] we supply evidence for the whole reversible sequence I ⇄ V.[5]

1-Acetyl-2,2-dimethylcyclopropane (VI, R = Me) smoothly rearranged to (β-methylallyl)acetone (VII, R = Me) at temperatures above 150°. First-order rate constants of 3.86×10^{-5} sec.$^{-1}$ (152°) and $9.00 \times$



10^{-5} sec.$^{-1}$ (163°) and an activation energy of 33 kcal./mole were calculated. The reaction mixtures were analyzed by vapor phase chromatography, and (β-methylallyl)acetone was found to be the only product that developed. A sample of the product was isolated from a rearrangement mixture by preparative scale v.p.c. and identified through its semicarbazone (m.p.

(1) W. M. Lauer and W. F. Filbert, *J. Am. Chem. Soc.*, **58**, 1388 (1936), and later papers.

(2) E. N. Marvell, D. R. Anderson, and J. Ong, *J. Org. Chem.*, **27**, 1109 (1962).

(3) A. Habich, R. Barner, R. M. Roberts, and H. Schmid, *Helv. Chim. Acta*, **45**, 1943 (1962).

(4) R. M. Roberts, R. N. Greene, R. G. Landolt, and E. W. Heyer, *J. Am. Chem. Soc.*, **87**, 2282 (1965).

(5) D. E. McGreer, N. W. K. Chiu, and R. S. McDaniel [*Proc. Chem. Soc.*, 415 (1964)] recently observed thermal isomerizations of several esters, which they explained in terms of the mechanism represented by the sequence III → I, where A = OCH_3. R. J. Ellis and H. M. Frey [*ibid.*, 221 (1964)] described a similar rearrangement of *cis*-1-methyl-2-vinylcyclopropane. None of these compounds was structurally capable of showing rearrangement of the type I → V.